Supporting Information

Ring-closing Reaction of Allenic/propargylic Anions Generated by Base Treatment of Sulfonylallenes

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General. Melting points are uncorrected. IR spectra were measured in CHCl_3 . ^1H NMR spectra were taken in CDCl_3 . CHCl_3 (7.26 ppm) for silyl compounds and tetramethylsilane (0.00 ppm) for compounds without a silyl group were used as internal standards. ^{13}C NMR spectra were recorded in CDCl_3 with CDCl_3 (77.00 ppm) as an internal standard. All reactions were carried out under a nitrogen atmosphere. Silica gel (silica gel 60, 230-400 mesh) was used for chromatography. Organic extracts were dried over anhydrous Na_2SO_4 .

Typical Procedure for Preparation of (Phenylsulfonyl)alkadienyl *p*-toluenesulfonate:

Preparation of 3-(Phenylsulfonyl)penta-3,4-dienyl *p*-toluenesulfonate (6a). To a solution of 3-(phenylsulfonyl)penta-3,4-dien-1-ol¹ (51.2 mg, 0.229 mmol) in CH_2Cl_2 (2.3 mL) were added Et_3N (0.19 mL, 1.4 mmol) and TsCl (131 mg, 0.686 mmol) at 0 °C. After the mixture was stirred at room temperature for 10 h, the reaction was quenched by addition of saturated aqueous NaHCO_3 , and the mixture was extracted with AcOEt . The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane– AcOEt (2:1) afforded **6a** (75.3 mg, 87%) as a colorless oil; IR 1971, 1934 cm^{-1} ; ^1H NMR δ 7.87–7.83 (2H, m), 7.74–7.71 (2H, m), 7.68–7.52 (3H, m), 7.35 (2H, d, J = 8.3 Hz), 5.36 (2H, t, J = 3.0 Hz), 4.12 (2H, t, J = 6.7 Hz), 2.61 (2H, tt, J = 6.7, 3.0 Hz), 2.46 (3H, s); ^{13}C NMR δ 207.9, 145.0, 139.4, 133.7, 132.6, 129.8, 129.1, 128.0, 127.8, 108.4, 85.1, 67.0, 26.8, 21.6; MS m/z 378 (M^+ , 6.0); HRMS calcd for $\text{C}_{18}\text{H}_{18}\text{O}_5\text{S}_2$ 378.0596, found 378.0602.

6-(Phenylsulfonyl)octa-6,7-dienyl *p*-toluenesulfonate (6b). According to the above procedure, **6b** (100 mg, 91%) was obtained from 6-(phenylsulfonyl)octa-6,7-dien-1-ol¹ (69.6 mg, 0.262 mmol) as a colorless oil; IR 1969, 1940 cm^{-1} ; ^1H NMR δ 7.88 (2H, d, J = 8.3 Hz), 7.77 (2H, d, J = 8.3 Hz), 7.63–7.61 (1H, m), 7.56–7.53 (2H, m), 7.34 (2H, d, J = 8.3 Hz), 5.34 (2H, t, J = 3.4 Hz), 3.97 (2H, t, J = 6.3 Hz), 2.45 (3H, s), 2.20 (2H, tt, J = 6.8, 3.4 Hz), 1.59 (2H, quin, J = 6.3 Hz), 1.41 (2H, quin, J = 6.3 Hz), 1.33–1.28 (2H, m); ^{13}C NMR δ 207.6, 144.7, 140.0, 133.5, 133.0, 129.8, 129.1, 128.0, 127.8, 112.9, 84.5, 70.1, 28.4, 26.7, 26.4, 24.5, 21.6; MS m/z 420 (M^+ , 92.3); HRMS calcd for $\text{C}_{21}\text{H}_{24}\text{O}_5\text{S}_2$ 420.1065, found 420.1060.

Typical Procedure for Preparation of Iodo(phenylsulfonyl)alkadiene: Preparation of 8-

Iodo-3-(phenylsulfonyl)octa-1,2-diene (6b'). To a solution of **6b** (164 mg, 0.390 mmol) in acetone (3.9 mL) was added NaI (117 mg, 0.780 mmol), and the mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature, diluted with water, and extracted with AcOEt . The extract was washed with water and brine, dried, and concentrated to dryness.

Chromatography of the residue with hexane–AcOEt (5:1) afforded **6b'** (125 mg, 85%) as a colorless oil; IR 1969, 1940 cm^{-1} ; ^1H NMR δ 7.91–7.88 (2H, m), 7.67–7.52 (3H, m), 5.38 (2H, t, $J = 3.5$ Hz), 3.13 (2H, t, $J = 6.9$ Hz), 2.28–2.22 (2H, m), 1.75 (2H, quin, $J = 6.9$ Hz), 1.52–1.31 (4H, m); ^{13}C NMR δ 207.6, 140.0, 133.4, 129.0, 128.0, 113.0, 84.5, 32.8, 29.4, 26.4, 26.2, 6.6; MS m/z 376 (M^+ , 24.6); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{O}_2\text{IS}$ 375.9994, found 376.0004.

7-Iodo-3-(phenylsulfonyl)hepta-1,2-diene (6c). According to the above procedure, **6c** (90.0 mg, 80% for 2 steps) was obtained from 5-(phenylsulfonyl)hepta-5,6-dien-1-ol¹ (78.5 mg, 0.311 mmol) as a colorless oil; IR 1969, 1938 cm^{-1} ; ^1H NMR δ 7.91–7.87 (2H, m), 7.67–7.52 (3H, m), 5.40 (2H, t, $J = 3.5$ Hz), 3.11 (2H, t, $J = 6.9$ Hz), 2.27 (2H, tt, $J = 6.9, 3.5$ Hz), 1.79 (2H, quin, $J = 6.9$ Hz), 1.56 (2H, quin, $J = 6.9$ Hz); ^{13}C NMR δ 207.5, 139.9, 133.5, 129.0, 127.9, 112.6, 84.6, 32.2, 28.0, 25.4, 5.8; MS m/z 361 (M^+ , 6.7); HRMS calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2\text{IS}$ 361.9838, found 361.9842.

6-Iodo-3-(phenylsulfonyl)hexa-1,2-diene (6d). According to the above procedure, **6d** (70.4 mg, 80% for 2 steps) was obtained from 4-(phenylsulfonyl)hexa-4,5-dien-1-ol¹ (60.2 mg, 0.253 mmol) as a colorless oil; IR 1969, 1938 cm^{-1} ; ^1H NMR δ 7.87–7.84 (2H, m), 7.63–7.48 (3H, m), 5.36 (2H, t, $J = 3.3$ Hz), 3.09 (2H, t, $J = 6.8$ Hz), 2.33 (2H, tt, $J = 6.8, 3.3$ Hz), 1.92 (2H, quin, $J = 6.9$ Hz); ^{13}C NMR δ 207.5, 139.8, 133.6, 129.1, 128.0, 111.7, 84.7, 31.0, 27.7, 4.4; MS m/z 347 (M^+ , 4.0); HRMS calcd for $\text{C}_{12}\text{H}_{13}\text{O}_2\text{IS}$ 347.9681, found 347.9694.

9-Iodo-3-(phenylsulfonyl)nona-1,2-diene (6e). According to the above procedure, **6e** (20.9 mg, 82% for 2 steps) was obtained from 7-(phenylsulfonyl)nona-7,8-dien-1-ol (18.3 mg, 6.54×10^{-2} mmol) as a colorless oil; IR 1969, 1942 cm^{-1} ; ^1H NMR δ 7.91–7.88 (2H, m), 7.67–7.52 (3H, m), 5.37 (2H, t, $J = 3.4$ Hz), 3.14 (2H, t, $J = 6.9$ Hz), 2.23 (2H, tt, $J = 6.9, 3.4$ Hz), 1.77 (2H, quin, $J = 6.9$ Hz), 1.47–1.23 (6H, m); ^{13}C NMR δ 207.7, 140.1, 133.4, 129.0, 128.0, 113.2, 84.4, 33.2, 30.0, 27.6, 27.1, 26.5, 6.9; MS m/z 390 (M^+ , 38.9); HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{O}_2\text{IS}$ 390.0151, found 390.0167.

Typical Procedure for Preparation of (Phenylsulfonyl)alkadienal 8: Preparation of 6-(Phenylsulfonyl)octa-6,7-dien-1-al (8a). To a solution of 6-(phenylsulfonyl)octa-6,7-dien-1-ol (106 mg, 0.400 mmol) in CH_2Cl_2 (4.0 mL) was added Dess-Martin periodinane (339 mg, 0.800 mmol) at 0 °C. After the mixture was stirred at that temperature for 30 min, the reaction was quenched with saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and NaHCO_3 , and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (2:1) afforded **8a** (100 mg, 94%) as a colorless oil; IR 1971, 1938, 1722 cm^{-1} ; ^1H NMR δ 9.72 (1H, t, $J = 1.5$ Hz), 7.91–7.88 (2H, m), 7.67–7.52 (3H, m), 5.37 (2H, t, $J = 3.5$ Hz), 2.40 (2H, td, $J = 7.1, 1.5$ Hz), 2.27 (2H, tt, $J = 7.1,$

3.5 Hz), 1.67–1.43 (4H, m); ^{13}C NMR δ 207.6, 201.9, 140.0, 133.5, 129.1, 128.1, 112.9, 84.5, 43.3, 26.8, 26.4, 21.1; MS m/z 264 (M^+ , 20.2); HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$ 264.0820, found 264.0818.

5-(Phenylsulfonyl)hepta-5,6-dien-1-al (8b). According to the above procedure, **8b** (27.2 mg, 80%) was obtained from 5-(phenylsulfonyl)hepta-5,6-dien-1-ol (34.0 mg, 0.135 mmol) as a colorless oil; IR 1971, 1940, 1724 cm^{-1} ; ^1H NMR δ 9.71 (1H, s), 7.89 (2H, d, $J = 7.6$ Hz), 7.64 (1H, t, $J = 7.3$ Hz), 7.55 (2H, t, $J = 7.3$ Hz), 5.40 (2H, t, $J = 3.3$ Hz), 2.46 (2H, t, $J = 7.1$ Hz), 2.29 (2H, tt, $J = 7.1, 3.3$ Hz), 1.80 (2H, quin, $J = 7.1$ Hz); ^{13}C NMR δ 207.6, 201.2, 139.9, 133.6, 129.1, 128.1, 112.6, 84.8, 42.6, 26.0, 19.9; MS m/z 250 (M^+ , 30.5); HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}$ 250.0664, found 250.0667.

Methyl 8-(phenylsulfonyl)deca-2,8,9-trienoate (11). To a solution of 8-(*tert*-butyldimethylsiloxy)oct-2-yn-1-ol (**i**)¹ (430 mg, 1.68 mmol) in THF (15 mL) were added $i\text{Pr}_2\text{NEt}$ (0.90 mL, 5.0 mmol) and a solution of PhSOCl (403 mg, 2.52 mmol) in THF (2 mL) at -78°C . After the mixture was stirred at that temperature for 1 h, the reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (5:1) to afford the crude sulfinate (673 mg) as a colorless oil. The sulfinate was dissolved in MeOH (17 mL), and PPTS (42.2 mg, 0.168 mmol) was added at room temperature. After being stirred for 4 h, the mixture was concentrated and the residue was partitioned between AcOEt and water. The aqueous layer was extracted with AcOEt, and the combined extracts were washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (1:1) afforded 8-(phenylsulfonyloxy)oct-6-yn-1-ol (**ii**) (418 mg, 94% for 2 steps) as a colorless oil; IR 3628, 3481, 2235 cm^{-1} ; ^1H NMR δ 7.75–7.73 (2H, m), 7.58–7.52 (3H, m), 4.62 (1H, dt, $J = 15.1, 2.2$ Hz), 4.34 (1H, dt, $J = 15.1, 2.2$ Hz), 3.63 (2H, t, $J = 6.6$ Hz), 2.20 (2H, tt, $J = 6.8, 2.2$ Hz), 1.91 (1H, s), 1.57–1.42 (6H, m); ^{13}C NMR δ 144.2, 132.3, 129.0, 125.2, 89.2, 74.0, 62.4, 53.1, 32.0, 27.9, 24.9, 18.6; MS m/z 266 (M^+ , 11.9); HRMS calcd for $\text{C}_{14}\text{H}_{18}\text{O}_3\text{S}$ 266.0977, found 266.0981.

To a solution of **ii** (196 mg, 0.737 mmol) in AcOEt (7.4 mL) was added IBX (619 mg, 2.21 mmol) at room temperature, and the mixture was heated at 80°C for 1 h. The reaction mixture was cooled

to room temperature and filtered. The filtrate was concentrated, and the residue was passed through a short pad of silica gel with hexane–AcOEt (3:2) to afford the crude aldehyde (150 mg) as a colorless oil. To a solution of trimethyl phosphonoacetate (148 mg, 0.811 mmol) in THF (7.4 mL) was gradually added *n*BuLi (1.40 M in hexane, 0.53 mL, 0.74 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min. A solution of the crude aldehyde (150 mg) in THF (3.7 mL) was added to the mixture, and stirring was continued for 30 min. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (3:1) afforded methyl (*E*)- and (*Z*)-10-(phenylsulfinyloxy)-dec-2-en-8-ynoate (81.9 mg, 35% and 49.1 mg, 21%).

To a solution of (*E*)-ester (70.0 mg, 0.218 mmol) in toluene (2.2 mL) was added [RhCl(CO)₂]₂ (4.2 mg, 0.011 mmol) at room temperature, and the mixture was stirred at that temperature for 2 h.² Toluene was evaporated off, and the residue was chromatographed with hexane–AcOEt (2:1) to afford (*E*)-**11** (38.5 mg, 55%) as a colorless oil; IR 1971, 1940, 1717, 1659 cm⁻¹; ¹H NMR δ 7.91–7.87 (2H, m), 7.67–7.52 (3H, m), 6.88 (1H, dt, *J* = 15.6, 6.9 Hz), 5.77 (1H, d, *J* = 15.6 Hz), 5.37 (2H, t, *J* = 3.4 Hz), 3.72 (3H, s), 2.25–2.23 (2H, m), 2.18–2.11 (2H, m), 1.46–1.44 (4H, m); ¹³C NMR δ 207.6, 166.9, 148.7, 140.1, 133.5, 129.0, 128.0, 121.2, 113.0, 84.4, 51.4, 31.6, 27.0, 26.7, 26.3; MS *m/z* 320 (M⁺, 39.1); HRMS calcd for C₁₇H₂₀O₄S 320.1082, found 320.1087.

According to the above procedure, (*Z*)-**11** (18.6 mg, 45%) was obtained from (*Z*)-10-(phenylsulfinyloxy)-dec-2-en-8-ynoate (41.6 mg, 0.130 mmol) as a colorless oil; IR 1971, 1940, 1717, 1645 cm⁻¹; ¹H NMR δ 7.89 (2H, d, *J* = 7.4 Hz), 7.63 (1H, t, *J* = 7.4 Hz), 7.54 (2H, t, *J* = 7.4 Hz), 6.14 (1H, dt, *J* = 11.5, 7.4 Hz), 5.76 (1H, d, *J* = 11.5 Hz), 5.36 (2H, t, *J* = 3.5 Hz), 3.69 (3H, s), 2.60 (2H, q, *J* = 6.8 Hz), 2.26–2.22 (2H, m), 1.53–1.40 (4H, m); ¹³C NMR δ 207.7, 166.7, 149.9, 140.1, 133.4, 129.0, 128.1, 119.6, 113.1, 84.4, 51.0, 28.4, 28.1, 27.0, 26.4; MS *m/z* 320 (M⁺, 1.3); HRMS calcd for C₁₇H₂₀O₄S 320.1082, found 320.1089.

6-Iodo-1-phenyl-2-vinylidenehexan-1-one (13a). To a solution of 7-(*tert*-butyldimethylsiloxy)hept-2-yn-1-ol (**iii**)¹ (410 mg, 1.69 mmol) in CH₂Cl₂ (17 mL) were added CBr₄ (674 mg, 2.03 mmol) and PPh₃ (487 mg, 1.86 mmol) at 0 °C, and the mixture was stirred at that temperature for 30 min. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (50:1) to afford the crude bromide (470 mg) as a pale yellow oil. The bromide was dissolved in DMF (2.0 mL), and SnCl₂ (417 mg, 2.20 mmol) and NaI (304 mg, 2.03 mmol) were added at room temperature.³ After being stirred for 1 h, the reaction mixture was cooled to 0 °C, and a solution of benzaldehyde (197 mg, 1.86 mmol) in DMF (1.0 mL) was added. After stirring for 6 h, the reaction was quenched by addition of water, and the mixture was extracted with Et₂O. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (10:1) to afford the crude allenyl alcohol (74.0 mg) as a pale yellow oil. The allenyl alcohol was dissolved in DMSO (2.4 mL), and IBX (197 mg, 0.705 mmol) was added at room temperature. After being stirred for 3 h, the reaction mixture was diluted with water and extracted with Et₂O. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (8:1) afforded 6-(*tert*-butyldimethylsiloxy)-1-phenyl-2-vinylidenehexan-1-one (**iv**) (68.5 mg, 12% for 3 steps) as a colorless oil; IR 1960, 1931, 1649 cm⁻¹; ¹H NMR δ 7.76 (2H, d, *J* = 7.3 Hz), 7.50 (1H, t, *J* = 7.3 Hz), 7.38 (2H, t, *J* = 7.3 Hz), 5.05 (2H, t, *J* = 2.6 Hz), 3.64 (2H, t, *J* = 6.0 Hz), 2.45–2.42 (2H, m), 1.66–1.54 (4H, m), 0.89 (9H, s), 0.05 (6H, s); ¹³C NMR δ 217.0, 194.8, 138.4, 132.0, 129.0, 127.8, 106.8, 79.5, 62.9, 32.4, 27.6, 26.0, 24.2, 18.3, –5.3; MS *m/z* 330 (M⁺, 14.5); HRMS calcd for C₂₀H₃₀O₂Si 330.2015, found 330.2007.

To a solution of **iv** (73.0 mg, 0.221 mmol) in MeOH (2.2 mL) was added PPTS (5.6 mg, 2.2 × 10⁻²

mmol) at room temperature, and the mixture was stirred for 5 h. The mixture was concentrated, and the residue was partitioned between AcOEt and water. The aqueous layer was extracted with AcOEt, and the combined extracts were washed with water and brine, dried, and concentrated to dryness. The residue was dissolved in CH₂Cl₂ (2.2 mL), and Et₃N (0.19 mL, 1.4 mmol) and TsCl (126 mg, 0.663 mmol) were added at 0 °C. After the mixture was stirred at room temperature for 10 h, the reaction was quenched by addition of saturated aqueous NaHCO₃, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (5:1) to afford the crude tosylate (70.0 mg) as a colorless oil. To a solution of the tosylate in acetone (2.2 mL) was added NaI (66.3 mg, 0.442 mmol), and the mixture was refluxed for 1 h. The reaction mixture was cooled to room temperature, diluted with water, and extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. Chromatography of the residue with hexane–AcOEt (10:1) afforded **13a** (48.2 mg, 67% for 3 steps) as a colorless oil; IR 1960, 1931, 1649 cm⁻¹; ¹H NMR δ 7.77–7.73 (2H, m), 7.53–7.48 (1H, m), 7.42–7.36 (2H, m), 5.10 (2H, t, *J* = 2.8 Hz), 3.23 (2H, t, *J* = 6.9 Hz), 2.43 (2H, tt, *J* = 7.6, 2.8 Hz), 1.93 (2H, quin, *J* = 6.9 Hz), 1.64 (2H, quin, *J* = 6.9 Hz); ¹³C NMR δ 216.9, 194.6, 138.2, 132.1, 129.0, 127.9, 106.3, 79.8, 33.0, 28.7, 26.7, 6.5; MS *m/z* 326 (M⁺, 16.1); HRMS calcd for C₁₄H₁₅OI 326.0168, found 326.0165.

Methyl 6-iodo-2-vinylidenehexanoate (13b). To a solution of **iii** (196 mg, 0.810 mmol) in CH₂Cl₂ (8.1 mL) were added pyridine (0.20 mL, 2.4 mmol) and ClCO₂Me (0.07 mL, 0.9 mmol) at 0 °C. After the mixture was stirred at room temperature for 12 h, the reaction was quenched by addition of saturated aqueous NaHCO₃, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (5:1) to afford the crude carbonate (228 mg) as a colorless oil. To a solution of the crude carbonate in MeOH (1.4 mL) were added Pd(OAc)₂ (8.2 mg, 3.7 x 10⁻² mmol) and PPh₃ (38.4 mg, 0.147 mmol). After the mixture was stirred at 50 °C under 10 atm of CO for 10 h,⁴ the reaction mixture was filtered. The filtrate was concentrated to dryness, and the residue was chromatographed with hexane–AcOEt (20:1) to afford the allene **v** (109 mg, 49% for 2 steps) as a colorless oil; IR 1965, 1936, 1713 cm⁻¹; ¹H NMR δ 5.13 (2H, t, *J* = 3.0 Hz), 3.74 (3H, s), 3.61 (2H, t, *J* = 6.2 Hz), 2.28–2.20 (2H, m), 1.58–1.47 (4H, m), 0.88 (9H, s), 0.03 (6H, s); ¹³C NMR δ 213.9, 167.7, 100.0, 79.4, 62.9, 52.2, 32.2, 27.7, 25.9, 24.2, 18.3, –5.3; MS *m/z* 284 (M⁺, 5.6); HRMS calcd for C₁₅H₂₈O₃Si 284.1808, found 284.1806.

According to the procedure for preparation of **13a** from **iv**, **13b** (85.5 mg, 83% for 3 steps) was obtained from **v** (105 mg, 0.370 mmol) as a colorless oil; IR 1965, 1936, 1713 cm⁻¹; ¹H NMR δ

5.17 (2H, t, $J = 3.0$ Hz), 3.75 (3H, s), 3.20 (2H, t, $J = 6.9$ Hz), 2.27 (2H, tt, $J = 7.4, 3.0$ Hz), 1.88 (2H, quin, $J = 6.9$ Hz), 1.58 (2H, quin, $J = 7.4$ Hz); ^{13}C NMR δ 213.7, 167.4, 99.4, 79.3, 52.2, 32.7, 28.7, 26.9, 6.3; MS m/z 280 (M^+ , 11.1); HRMS calcd for $\text{C}_9\text{H}_{13}\text{O}_2\text{I}$ 279.9961, found 279.9965.

7-Iodo-3-(phenylmethyl)hepta-1,2-diene (13c). To a solution of **iii** (850 mg, 3.51 mmol) in CH_2Cl_2 (17 mL) were added Et_3N (1.00 mL, 7.1 mmol) and MsCl (0.41 mL, 5.3 mmol) at 0 °C. After the mixture was stirred at that temperature for 10 min, the reaction was quenched by addition of saturated aqueous NaHCO_3 , and the mixture was extracted with AcOEt . The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane– AcOEt (3:1) to afford the crude mesylate (914 mg) as a colorless oil. To a solution of CuBr (316 mg, 2.20 mmol) and LiBr (191 mg, 2.20 mmol) in THF (4.0 mL) was added BnMgCl (1.07 M in THF, 2.06 mL, 2.20 mmol) at –60 °C, and the mixture was stirred at that temperature for 30 min. A solution of the crude mesylate (588 mg) in THF (2.0 mL) was added dropwise to the mixture, which was stirred at that temperature for 15 min and at room temperature for 2 h. The reaction was quenched by addition of saturated aqueous NH_4Cl , and the mixture was extracted with AcOEt . The extract was washed with water and brine, dried, and concentrated to dryness. The residue was chromatographed with hexane– AcOEt (50:1) to afford the allene **vi** (380 mg, 53% for 2 steps) as a colorless oil; IR 1958 cm^{-1} ; ^1H NMR δ 7.31–7.19 (5H, m), 4.66 (2H, tt, $J = 3.3, 2.5$ Hz), 3.57 (2H, t, $J = 6.2$ Hz), 3.29 (2H, t, $J = 2.5$ Hz), 1.90 (2H, tt, $J = 6.9, 3.3$ Hz), 1.53–1.42 (4H, m), 0.88 (9H, s), 0.03 (6H, s); ^{13}C NMR δ 206.7, 139.7, 128.8, 128.2, 126.1, 102.6, 75.3, 63.0, 39.5, 32.3, 30.8, 26.0, 23.7, 18.4, –5.3; MS m/z 316 (M^+ , 43.4); HRMS calcd for $\text{C}_{20}\text{H}_{32}\text{OSi}$ 316.2223, found 316.2232.

According to the procedure for preparation of **13a** from **iv**, **13c** (214 mg, 70% for 3 steps) was obtained from **vi** (310 mg, 0.981 mmol) as a colorless oil; IR 1958 cm^{-1} ; ^1H NMR δ 7.32–7.18 (5H, m), 4.69 (2H, tt, $J = 3.3, 2.5$ Hz), 3.29 (2H, t, $J = 2.5$ Hz), 3.14 (2H, t, $J = 7.0$ Hz), 1.90 (2H, tt, $J = 7.0, 3.3$ Hz), 1.81 (2H, quin, $J = 7.0$ Hz) 1.57–1.47 (2H, m); ^{13}C NMR δ 206.6, 139.4, 128.9, 128.2, 126.2, 102.0, 75.6, 39.5, 32.9, 29.8, 28.1, 6.8; MS m/z 312 (M^+ , 27.5); HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{I}$ 312.0375, found 312.0368.

General procedure for ring-closing reaction. To a solution of allene (0.1 mmol) in solvent (1 mL) was added base (0.2 mmol). After being stirred for 30 min, the reaction mixture was quenched by addition of water and extracted with Et_2O . The extract was washed with water and brine, dried and concentrated to dryness. The residue was chromatographed with hexane– AcOEt .

1-Ethynyl-1-(phenylsulfonyl)cyclopropane (7a). Colorless needles: m.p. 92.5–93 °C (hexane): IR 3306 cm^{-1} ; ^1H NMR δ 7.98–7.95 (2H, m), 7.72–7.55 (3H, m), 2.22 (1H, s), 1.84 (2H, dd, $J = 7.4$,

4.3 Hz), 1.40 (2H, dd, $J = 7.4, 4.3$ Hz); ^{13}C NMR δ 138.0, 133.9, 129.0, 128.9, 78.9, 71.9, 35.0, 16.3; MS m/z 206 (M^+ , 78.9). Anal. Calcd for $\text{C}_{11}\text{H}_{10}\text{O}_2\text{S}$: C, 64.05; H, 4.89. Found: C, 64.00; H, 4.93.

1-Ethynyl-1-(phenylsulfonyl)cyclohexane (7b). Colorless needles: m.p. 138.5–139 °C (hexane): IR 3306 cm^{-1} ; ^1H NMR δ 8.00–7.95 (2H, m), 7.71–7.52 (3H, m), 2.51 (1H, s), 1.96–1.15 (10H, m); ^{13}C NMR δ 134.8, 133.9, 131.0, 128.4, 80.1, 77.4, 64.5, 30.4, 24.7, 22.2; MS m/z 248 (M^+ , 69.3); HRMS calcd for $\text{C}_{14}\text{H}_{16}\text{O}_2\text{S}$ 248.0871, found 248.0878.

1-Ethynyl-1-(phenylsulfonyl)cyclopentane (7c). Colorless needles: m.p. 126.5–127.5 °C (hexane): IR 3306 cm^{-1} ; ^1H NMR δ 8.04–7.99 (2H, m), 7.71–7.64 (1H, m), 7.59–7.52 (2H, m), 2.56–2.45 (2H, m), 2.47 (1H, s), 2.06–1.83 (6H, m); ^{13}C NMR δ 136.4, 133.9, 130.4, 128.5, 82.8, 75.1, 67.9, 36.2, 25.2; MS m/z 234 (M^+ , 21.2). Anal. Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{S}$: C, 66.64; H, 6.02. Found: C, 66.21; H, 5.99.

1-Ethynyl-1-(phenylsulfonyl)cyclobutane (7d). White solid: IR 3306 cm^{-1} ; ^1H NMR δ 7.98–7.94 (2H, m), 7.70–7.64 (1H, m), 7.58–7.53 (2H, m), 3.06–2.95 (2H, m), 2.56 (1H, s), 2.39–2.08 (4H, m); ^{13}C NMR δ 135.5, 134.0, 130.1, 128.7, 81.4, 76.2, 59.6, 30.5, 15.6; MS m/z 220 (M^+ , 27.9); HRMS calcd for $\text{C}_{12}\text{H}_{12}\text{O}_2\text{S}$ 220.0558, found 220.0560.

1-Ethynyl-1-(phenylsulfonyl)cycloheptane (7e). Colorless needles: m.p. 83–84 °C (hexane): IR 3304 cm^{-1} ; ^1H NMR δ 7.99 (2H, d, $J = 8.1$ Hz), 7.67 (1H, t, $J = 7.6$ Hz), 7.55 (2H, t, $J = 7.6$ Hz), 2.52 (1H, s), 2.17–2.07 (4H, m), 1.81–1.55 (8H, m); ^{13}C NMR δ 135.3, 133.9, 131.2, 128.4, 81.5, 76.7, 67.1, 33.7, 27.6, 23.1; MS m/z 262 (M^+ , 7.7). Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2\text{S}$: C, 68.67; H, 6.92. Found: C, 68.26; H, 6.92.

(1*R,2*R**)-2-Ethynyl-2-(phenylsulfonyl)cyclohexan-1-ol (cis-9a).** Colorless needles: IR 3529, 3304 cm^{-1} ; ^1H NMR δ 8.00–7.98 (2H, m), 7.71–7.68 (1H, m), 7.57 (2H, t, $J = 7.6$ Hz), 4.28 (1H, dt, $J = 11.0, 3.2$ Hz), 3.49 (1H, d, $J = 3.2$ Hz), 2.58 (1H, s), 2.03–1.99 (1H, m), 1.83–1.25 (7H, m); ^{13}C NMR δ 134.9, 134.3, 130.9, 128.5, 79.3, 76.9, 70.1, 69.8, 31.7, 31.5, 23.5, 21.7; MS m/z 264 (M^+ , 4.7). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$: C, 63.61; H, 6.10. Found: C, 63.30; H, 6.07.

(1*R,2*S**)-2-Ethynyl-2-(phenylsulfonyl)cyclohexan-1-ol (trans-9a).** Colorless needles: IR 3524, 3304 cm^{-1} ; ^1H NMR δ 7.99–7.96 (2H, m), 7.74–7.68 (1H, m), 7.57 (2H, t, $J = 7.4$ Hz), 4.23 (1H, brs), 3.97 (1H, brs), 2.55 (1H, s), 2.41 (1H, td, $J = 12.2, 3.5$ Hz), 1.89–1.44 (7H, m); ^{13}C NMR δ 134.4, 134.3, 130.8, 128.6, 79.5, 79.0, 68.2, 66.9, 29.5, 24.5, 21.9, 18.0; MS m/z 264 (M^+ , 3.6). Anal. Calcd for $\text{C}_{14}\text{H}_{16}\text{O}_3\text{S}$: C, 63.61; H, 6.10. Found: C, 63.46; H, 6.08.

2-Ethynyl-2-(phenylsulfonyl)cyclopentan-1-ol (9b). Colorless needles: IR 3566, 3304 cm^{-1} ; ^1H NMR δ 8.00–7.98 (2H, m), 7.71–7.67 (1H, m), 7.59–7.56 (2H, m), 4.79 (1H, td, $J = 7.6, 5.4$ Hz), 2.61 (1H, s), 2.55–2.49 (1H, m), 2.38 (1H, d, $J = 5.4$ Hz), 2.26–2.22 (1H, m), 2.08–2.02 (1H, m), 1.90–1.74 (3H, m); ^{13}C NMR δ 136.0, 134.2, 130.3, 128.7, 79.2, 78.1, 75.1, 71.9, 34.2, 32.6, 19.6;

MS m/z 250 (M^+ , 86.9). Anal. Calcd for $C_{13}H_{14}O_3S$: C, 62.38; H, 5.64. Found: C, 62.13; H, 5.62.

2-Methyl-3-(phenylsulfonyl)cyclopent-1-enecarbaldehyde (10). A pale yellow oil: IR 1672, 1636 cm^{-1} ; 1H NMR δ 10.03 (1H, s), 7.88–7.86 (2H, m), 7.69–7.66 (1H, m), 7.57–7.54 (2H, m), 4.28 (1H, d, J = 9.5 Hz), 2.41 (3H, s), 2.41–2.36 (1H, m), 2.31–2.26 (1H, m), 2.16–2.01 (2H, m); ^{13}C NMR δ 187.7, 150.5, 144.4, 137.3, 134.2, 129.2, 128.8, 77.4, 28.4, 25.1, 14.2; MS m/z 250 (M^+ , 74.4); HRMS calcd for $C_{13}H_{14}O_3S$ 250.0664, found 250.0669.

Methyl 2-ethynyl-2-(phenylsulfonyl)cyclohexaneacetate (12). A 5:1~30:1 mixture of *cis*-**12** and *trans*-**12** was obtained as a white solid: 3304, 1732 cm^{-1} ; 1H NMR data for *cis*-**12**: δ 7.96 (2H, d, J = 7.9 Hz), 7.67 (1H, t, J = 7.9 Hz), 7.56 (2H, t, J = 7.9 Hz), 3.70 (3H, s), 3.60 (1H, dd, J = 16.5, 3.4 Hz), 2.68 (1H, tt, J = 11.0, 3.4 Hz), 2.64 (1H, s), 2.39 (1H, dd, J = 16.5, 11.0 Hz), 1.85–1.83 (1H, m), 1.75 (1H, td, J = 12.8, 3.4 Hz), 1.65–1.54 (3H, m), 1.50–1.32 (2H, m), 1.27–1.19 (1H, m); ^{13}C NMR data for *cis*-**12**: δ 172.6, 135.9, 134.0, 130.7, 128.6, 78.8, 77.7, 67.5, 51.6, 37.6, 36.7, 34.4, 29.9, 24.6, 22.3; characteristic NMR data for *trans*-**12**: 1H NMR δ 3.36 (1H, d, J = 14.6 Hz), 2.81–2.77 (1H, m), 2.51 (1H, s), 2.09–2.04 (1H, m); ^{13}C NMR δ 130.9, 128.4, 81.6, 78.2, 66.6, 51.7, 33.3, 27.1, 21.7, 20.1; MS m/z 320 (M^+ , 27.5); HRMS calcd for $C_{17}H_{20}O_4S$ 320.1082, found 320.1087.

1-Ethynylcyclopentyl phenyl ketone (14a). A colorless oil: IR 3306, 2110, 1680 cm^{-1} ; 1H NMR δ 8.24–8.21 (2H, m), 7.57–7.41 (3H, m), 2.45–2.35 (2H, m), 2.40 (1H, s), 2.22–2.13 (2H, m), 1.95–1.80 (2H, m), 1.75–1.65 (2H, m); ^{13}C NMR δ 197.2, 134.8, 132.7, 130.0, 128.0, 88.2, 72.8, 51.6, 39.0, 25.1; MS m/z 198 (M^+ , 66.7); HRMS calcd for $C_{14}H_{14}O$ 198.1045, found 198.1047.

Methyl 1-ethynylcyclopentanecarboxylate (14b). A colorless oil: IR 3306, 2116, 1732 cm^{-1} ; 1H NMR δ 3.77 (3H, s), 2.30 (1H, s), 2.24–2.18 (2H, m), 2.08–2.03 (2H, m), 1.87–1.73 (4H, m); ^{13}C NMR δ 173.7, 86.0, 70.3, 52.8, 47.9, 39.2, 24.7; MS m/z 152 (M^+ , 22.8); HRMS calcd for $C_9H_{12}O_2$ 152.0837, found 152.0844.

Stereochemical Assignments of 9a.

Transformation of 9a to 2-(Phenylsulfonyl)-2-ethenylcyclohexyl acetate. To a solution of *cis*-

9a (15.3 mg, 5.78×10^{-2} mmol) in pyridine (0.60 mL) were added Ac₂O (0.01 mL, 0.1 mmol) and 4-DMAP (1.4 mg, 1.2×10^{-2} mmol) at room temperature, and the mixture was stirred for 24 h. The reaction was quenched by addition of water, and the mixture was extracted with AcOEt. The extract was washed with water and brine, dried, and concentrated to dryness. The residue was passed through a short pad of silica gel with hexane–AcOEt (3:2) to afford the crude acetate (16.0 mg) as a colorless oil. The acetate was dissolved in MeOH (0.6 mL), and Lindlar catalyst (12.3 mg, 0.116 mmol) was added. After being stirred under H₂ atmosphere for 80 h, the reaction mixture was filtered, and the filtrate was concentrated to dryness. The residue was chromatographed with hexane–AcOEt (2:1) to afford (1*R**,2*S**)-2-(phenylsulfonyl)-2-ethenylcyclohexyl acetate (9.8 mg, 55% for 2 steps) as a white solid; IR 1738 cm⁻¹; ¹H NMR (C₆D₆) δ 7.80 (2H, dd, *J* = 7.7, 1.5 Hz), 6.93–6.85 (3H, m), 6.05 (1H, dd, *J* = 18.0, 11.0 Hz), 5.75 (1H, dd, *J* = 11.2, 4.3 Hz), 5.32 (1H, d, *J* = 11.0 Hz), 5.18 (1H, d, *J* = 18.0 Hz), 2.10–2.03 (1H, m), 1.88–1.84 (2H, m), 1.54 (3H, s), 1.18–0.90 (5H, m); ¹³C NMR δ 169.4, 137.6, 133.4, 130.7, 129.2, 128.4, 124.1, 72.4, 71.2, 29.0, 27.6, 23.8, 21.2, 20.8; MS *m/z* 308 (M⁺, 0.4); HRMS calcd for C₁₆H₂₀O₄S 308.1082, found 308.1088.

According to the above procedure, (1*R**,2*R**)-2-(phenylsulfonyl)-2-ethenylcyclohexyl acetate (10.3 mg, 67% for 2 steps) was obtained from *trans*-**9a** (13.3 mg, 5.02×10^{-2} mmol) as a white solid; IR 1740 cm⁻¹; ¹H NMR (C₆D₆) δ 7.74 (2H, dd, *J* = 7.6, 1.4 Hz), 6.98–6.87 (3H, m), 5.70 (1H, dd, *J* = 2.0, 1.8 Hz), 5.11 (1H, dd, *J* = 17.5, 11.0 Hz), 4.91 (1H, d, *J* = 11.0 Hz), 4.86 (1H, d, *J* = 17.5 Hz), 2.56 (1H, td, *J* = 12.8, 3.8 Hz), 1.87–1.70 (2H, m), 1.84 (3H, s), 1.44–1.00 (5H, m); MS *m/z* 308 (M⁺, 1.0); HRMS calcd for C₁₆H₂₀O₄S 308.1082, found 308.1084.

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